

PATENT SPECIFICATION

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640,127



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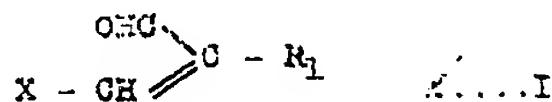
PROVISIONAL SPECIFICATION

Improvements in or relating to the Production of Cyanine
Dyestuffs and to the Sensitising of Photographic Emulsions

We, ILFORD LIMITED, a British Company, of 23, Eaden Street, Ilford, in the County of Essex, do hereby declare the nature of this invention to be as follows:—

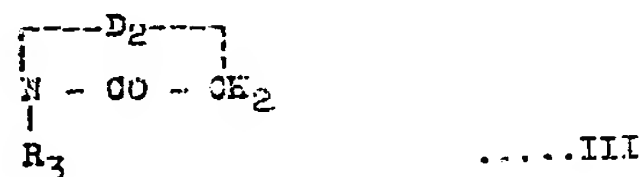
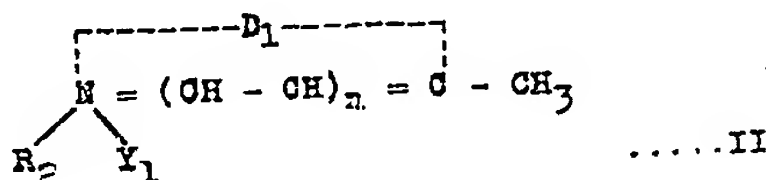
This invention relates to the production of cyanine dyestuffs and particularly to the production of symmetrical dicarbo-cyanine dyestuffs containing substituents in the polymethine chain. It further relates to the sensitising of photographic emulsions.

According to the present invention cyanine dyestuffs are prepared by condensing a compound of the general formula I:—



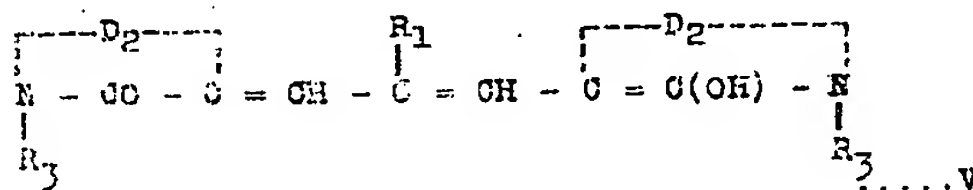
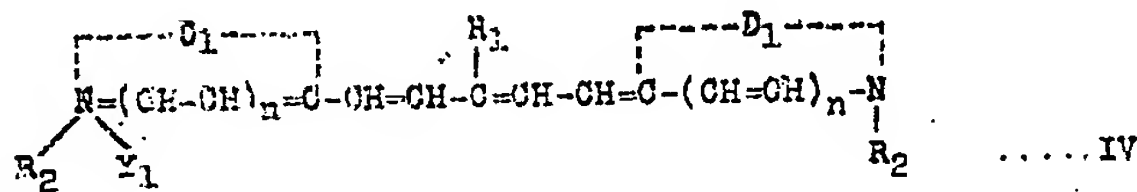
where R_1 is a nitrile (CN) or carboxylic ester (COOR) group and X is a thioether (—SR) or anil (NHR) group, R being a hydrocarbon group, with a heterocyclic nitrogen compound containing a reactive methylene group.

More particularly, according to this invention, the said heterocyclic compound conforms to one or other of the following general formulæ II and III:—



where R_2 is an alkyl, hydroxyalkyl or aralkyl group, Y_1 is an acid radicle, D_1 is the residue of a five-membered or six-membered heterocyclic ring, n is nought or one, R_3 is a hydrogen atom or an alkyl, aralkyl or aryl group and D_2 is the residue of a heterocyclic nitrogen-keto-methylene nucleus.

Accordingly as compounds of formulæ II or III are employed, so the products conform to formulæ IV or V:—



The condensation may be effected in the presence of a base or in the presence of an acid anhydride together with a base. A base such as pyridine is suitable, but

it is preferred to use a stronger base such as triethylamine or sodium acetate in conjunction with a carboxylic acid anhydride such as acetic anhydride.

As already indicated R_1 may be a nitrile group or a carboxylic ester group. Examples of the latter are groups of the form $-\text{COOR}$ where R is an alkyl, e.g. methyl, ethyl, propyl, butyl or higher alkyl group, an aralkyl group, e.g. benzyl or naphthylmethyl, or an aryl group, e.g. phenyl or naphthyl. R_2 may be any of the foregoing alkyl or aralkyl groups, or
 10 may be a hydroxyalkyl group such as β -hydroxy ethyl or γ -hydroxy propyl. Where R_2 is an hydroxyalkyl group this will usually be acylated by the acid condensing agent so that R_2 in the product
 15 will be an acyloxyalkyl group. R_3 , if not a hydrogen atom, may be any of the foregoing alkyl, aralkyl or aryl groups.

Y_1 may be any acid radicle, for example halide (chloride, bromide, iodide), sulphate, sulphonate, perchlorate or *p*-toluene sulphonate.
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D_1 may be the residue of any five-membered or six-membered heterocyclic ring system including thiazoles, oxazoles, selenazoles and their polycyclic homologues such as those of the benzene, naphthalene, acenaphthene and anthracene series; pyridine and its polycyclic homologues, such as quinoline and α - and β -naphthoquinolines; lepidines; indolenines; diazines such as pyrimidines and quinazolines; diazoles (e.g. thio- $\beta\beta'$ -diazole); oxazolines, thiazolines and selenazolines. The polycyclic compounds of these series may
 25 be substituted in the carbocyclic rings with one or more groups such as alkyl, aryl, amino, hydroxy, alkoxy and methylene dioxy groups, or by halogen atoms.

D_2 may be the residue of rhodanic acid (2-thio-4-keto-tetrahydrothiazole), oxarhodanic acid (2-thio-4-keto-tetrahydro-oxazole) and the *N*-hydrocarbon substituted derivatives of such compounds.
 30 oxindoles, pyrazole-5-ones, hydantoin, thio-hydantoin, pseudohydantoin and pseudothiohydantoin.

The initial starting compounds of general formula I may be prepared by reacting a compound of the formula $(\text{CH}_3)_2\text{C}=\text{CH}-\text{CN}$, i.e. acetonitrile or an acetic ester, with a formic ester (preferably ethyl formate) in the presence of powdered sodium. This yields the compound
 35 $R_1-\text{CH}_2-\text{CH}(\text{CO}_2\text{H})-\text{CH}_2-\text{CN}$ as its sodium salt. This product is then reacted with a mercaptan RSH in the presence of dry hydrochloric acid, or is reacted with aniline to produce the thioether or anil of the formula
 40 $R_1-\text{CH}_2-\text{CH}(\text{CN})-\text{CH}_2-\text{X}$. This latter compound is reacted further with a formic ester (preferably ethyl formate) and powdered sodium to yield a product of the formula I as required for use in the present
 45 invention.

Many of the dyestuffs formed according to this invention are sensitising dyes for silver halide photographic emulsions.

The following illustrate the preparation of compounds of general formula I:— 70

A. PREPARATION OF α -CARBETHIOXY MALON-DIALDEHYDE MONO ANIL.

10 parts of sodio formyl ethyl acetate were dissolved in 100 parts of water and added with stirring to a solution of 7 parts
 75 of aniline in a mixture of 40 parts of acetic acid and 160 parts of water. The ethyl-anilinomethylene acetate was precipitated as a flocculent yellow solid. M.pt. 105°.

This preparation is analogous to that of v. Pechmann, *Berichte der Deutschen Chemischen Gesellschaft*, 25, 1047.

A suspension of 30 parts of the above ethyl-anilinomethylene acetate in 100
 85 parts of dry ether and 11.7 parts of ethyl formate was added in portions to 3.62 parts of sodium powder under 200 parts of dry ether. A slight reaction ensued and afterwards the solution was refluxed
 90 for 8 hours and then poured into water under an atmosphere of CO_2 . The water was ether extracted, the extracts dried over sodium sulphate and the ether removed by distillation. The product was
 95 distilled under reduced pressure, b.pt. 197° at 8 mm. pressure to give an oil which solidified on cooling to a yellow crystalline mass.

B. PREPARATION OF ETHYL- α -FORMYL- β -ETHYLTHIO ACRYLATE.

14 parts of sodio formyl ethyl acetate and 25 parts of ethyl mercaptan were mixed together with 25 parts of dry ether, and dry HCl gas passed through
 105 the mixture for 2 hours with cooling. After being allowed to stand overnight, the solution was poured into dilute sodium carbonate solution, ether extracted, dried over sodium sulphate
 110 anhydrous, and the ether evaporated. Distillation under reduced pressure yielded β -ethylthio ethyl acrylate. B.pt. 160—165° at 30 mm. pressure.

11 parts of the above β -ethylthioethyl
 115 acrylate and 6 parts of ethyl formate were mixed with a little dry ether and reacted with 1.5 parts of sodium powder also under dry ether. After addition the mixture was heated for 24 hours and
 120 poured into water under an atmosphere of carbon dioxide. The aqueous liquors were acidified with acetic acid, ether extracted, the extracts being washed with water, dried and the ether removed by
 125 distillation. Distillation under reduced pressure yielded crude ethyl- α -formyl- β -

ethylthio acrylate. B.pt. 110—135° C. at 7 mm. pressure.

C. PREPARATION OF α -(*n*-PROPYL CARBOXY) MALONDIALDEHYDE MONO ANIL.

13 parts of sodio formyl-*n*-propyl acetate were dissolved in 60 parts of water and added with stirring to a solution of 8 parts of aniline in a mixture of 43 parts of acetic acid and 183 parts of water. The *n*-propyl-anilinomethylene acetate was precipitated as a slightly sticky yellow solid.

A suspension of 51 parts of the above *n*-propyl-anilinomethylene acetate in 100 parts of dry ether and 20 parts of ethyl formate was added in portions to 5 parts of sodium powder under 200 parts of dry ether. The mixture was refluxed for 8 hours and then poured into water under an atmosphere of CO₂. The ether was then evaporated and the product filtered from the aqueous solution. It was a yellow solid, m.pt. 132°.

D. PREPARATION OF α -CYANO-MALONDIALDEHYDE MONO ANIL.

30 parts of sodio formyl acetonitrile were dissolved in 267 parts of water and added with stirring to a solution of 30 parts of aniline in a mixture of 160 parts of acetic acid and 743 parts of water. The anilinomethylene acetonitrile was precipitated slowly as a yellow solid. M.pt. 119°.

A suspension of 7 parts of the above anilinomethylene acetonitrile, 30 parts of dry ether and 4 parts of ethyl formate was added in portions to 11 parts of sodium powder under 100 parts of dry ether. After complete addition the mixture was refluxed for 4 days and then poured into water under an atmosphere of CO₂. The ether was evaporated and the product filtered as a yellow solid. After crystallisation from ethyl alcohol it melted at 183°.

The following Examples serve to illustrate the invention.

EXAMPLE 1

BIS-2(3-ETHYL BENZTHIAZOLE)- γ -CARBOETHOXY PENTAMETHINE CYANINE IODIDE.

Method (i). 10 parts of α -carbethoxy malondialdehyde mono anil, 30 parts of 2-methyl benzthiazole ethiodide and 200 parts of pyridine were refluxed together for 3 minutes when the solution turned dark red. 6 parts of triethylamine were added with shaking and the solution allowed to cool before pouring into water. The dyestuff crystallised, was filtered and recrystallised from methyl alcohol to give dark green crystals. M.pt. 230° with decomposition.

Method (ii). 2 parts of ethyl- α -formyl- β -ethylthio acrylate, 6 parts of 2-methyl benzthiazole and 15 parts of 65 pyridine were heated together for 15 minutes, during which time a rich blue colour was formed. This solution was poured into water when the dyestuff crystallised as blue-green crystals. These 70 were well washed, dried and recrystallised from methyl alcohol. M.pt. 230° with decomposition.

This dyestuff, when incorporated in a gelatino silver bromide emulsion, im- 75 parts a band of sensitivity extending to 6800 Å with a maximum at 6460 Å.

EXAMPLE 2

BIS-2-(1-ETHYL QUINOLINE)- γ -CARBOETHOXY PENTAMETHINE CYANINE IODIDE. 80

10 parts of α -carbethoxy malondialdehyde mono anil, 30 parts of quinaldine ethiodide and 200 parts of pyridine were heated together for 3 minutes when the solution turned red-green. 6 parts of tri- 85 ethylamine were added and the solution refluxed for 30 minutes, during which time a green colour slowly appeared. The pyridine solution was poured into water when the dyestuff crystallised. Recrystal- 90 lisation from methyl alcohol gave blue-green crystals. M.pt. 253° (decomposition).

This dyestuff, when incorporated in a gelatino silver bromide emulsion, im- 95 parts a band of sensitivity extending to 7200 Å with a maximum at 6900 Å.

EXAMPLE 3

BIS-2-(1,3,3-TRIMETHYL-INDOLENINE)- γ -CARBOETHOXY PENTAMETHINE CYANINE IODIDE. 100

10 parts of α -carbethoxy malondialdehyde mono anil, 30 parts of 2,3,3-trimethyl indolenine methiodide and 200 parts of pyridine were reacted as in the 105 above Examples. The dyestuff was obtained as dark green-blue crystals upon dilution with water which, when recrystallised from methyl alcohol, melted at 207° (decomposition). 110

EXAMPLE 4

BIS-2(3- β -ACETOXYETHYL BENZTHIAZOLE)- γ -CARBOETHOXY PENTAMETHINE CYANINE IODIDE.

10 parts of α -carbethoxy malondialdehyde mono anil, 31.6 parts of 2-methyl benzthiazole β -hydroxy ethiodide and 100 parts of acetic anhydride were heated together for 2 minutes when the colour of the solution attained a deep red. The 120 solution was then cooled to 100°. 3 parts of triethylamine added with shaking, and the blue solution allowed to cool slowly. The dyestuff was obtained by precipita-

tion with ether, washing with water and subsequent treatment with acetone. The dark blue solid obtained melted at 110°.

EXAMPLE 5

5 BIS-2(3-3-ACETOXYETHYL-5 - CHLOR-BENZ-
THIAZOLE)-γ-CARBETHOXY PENTAMETHINE
CYANINE IODIDE.

10 10 parts of α-carbethoxy malondialde-
hyde mono anil, 34 parts of 2-methyl-5-
chlor - benzthiazole-β-hydroxy ethiodide
and 100 parts of acetic anhydride were
heated together and treated as in the
above Example. The dyestuff isolated as
previously was obtained as dark green
powdery crystals. M.pt. 154°.

EXAMPLE 6

BIS-2(3-3-ACETOXYETHYL BENZTHIAZOLE)-γ-
n - PROPYL CARBOXY PENTAMETHINE
CYANINE IODIDE.

20 2.55 parts of α-n-propyl carboxy malon-
dialdehyde mono anil, 3.1 parts of 2-
methyl benzthiazole-β-hydroxy ethiodide
and 20 parts of acetic anhydride were
heated together for 5 minutes. The solu-
tion was then cooled to 100°, 1.5 parts
of triethylamine added with shaking, and
the blue solution then cooled rapidly to
room temperature. Excess ether was
added to precipitate the dyestuff as a tar
which was washed with water and then
treated with acetone to give the crystal-
line dyestuff. This was recrystallised
from methyl alcohol to give dark blue-
green crystals. M.pt. 150° (decomposi-
tion).

This dyestuff, when incorporated in a
gelatine silver bromide emulsion, imparts
a weak band of sensitivity extending to
6600 Å with a maximum at 6500 Å.

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EXAMPLE 7

BIS-2(3-3-ACETOXYETHYL QUINOLINE)-γ-n-
PROPYL CARBOXY PENTAMETHINE CYANINE
IODIDE.

45 3.55 parts of α-n propyl carboxy
malondialdehyde mono anil, 3.1 parts of
quinoline-β-hydroxy ethiodide and 20
parts of acetic anhydride were heated
together and 1.5 parts of triethylamine
added. The procedure was similar to that
of the previous Example. The dyestuff
was obtained, after crystallisation from
methyl alcohol, as dark blue-green
crystals. M.pt. 124° (decomposition).

EXAMPLE 8

BIS-2(3-ETHYL BENZTHIAZOLE) - γ - CYANO 55
PENTAMETHINE CYANINE IODIDE.

1.7 parts of α-cyano-malondialdehyde
mono anil, 6 parts of 2-methyl benz-
thiazole ethiodide and 40 parts of acetic
anhydride were heated together for 5 60
minutes, during which time the colour
of the solution deepened to dark red. 1.6
parts of triethylamine were then added,
and after another 3 minutes' refluxing,
during which time a blue colour appeared, 65
the solution was cooled and the dyestuff
filtered. When recrystallised from methyl
alcohol it was obtained as dark brown
crystals with a green reflex. M.pt. 268°
(decomposition).

This dyestuff, when incorporated in a
gelatine silver bromide emulsion, imparts
a weak band of sensitivity extending to
6600 Å with a maximum at 6350 Å.

EXAMPLE 9

α,γ - BIS-3-(3-ETHYL-2-THIO-4-KETO - TETRA-
HYDROTHIAZOLE)-β-CYANO PROPENE. 75

1.7 parts of α-cyano-malondialdehyde
mono anil, 5.2 parts of N-ethyl rhodanic
acid and 40 parts of acetic anhydride were 80
heated together for 5 minutes. 1.4 parts
of triethylamine were then added and
heating continued for 15 minutes, during
which time the dye colour (dark green-
blue) gradually appeared. The solution 85
was cooled and the dyestuff filtered. Re-
crystallisation from methyl alcohol gave
blue crystals with a bright reflex. M.pt.
220° (decomposition).

EXAMPLE 10.

BIS-2(3-3-ACETOXYETHYL BENZTHIAZOLE)-
γ-CYANO PENTAMETHINE CYANINE IODIDE. 90

1.7 parts of α-cyano malondialdehyde
mono anil, 6.12 parts of 2-methyl benz-
thiazole-β-hydroxy ethiodide and 30 parts 95
of acetic anhydride were heated together
for 5 minutes, 1 part of triethylamine
added, and the solution refluxed for a
further 3 minutes. The dyestuff was
filtered, after cooling the solution, and 100
recrystallised from methyl alcohol when
it was obtained as dark blue crystals.
M.pt. 248° (decomposition).

Dated this 15th day of May, 1948.

V. GALLAFENT,
Chartered Patent Agent.

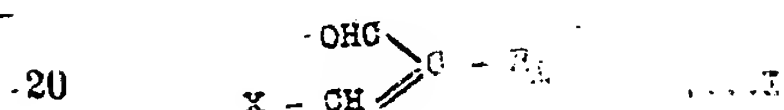
COMPLETE SPECIFICATION

Improvements in or relating to the Production of Cyanine Dyestuffs and to the Sensitising of Photographic Emulsions

We, ILFORD LIMITED, a British Company, of 23, Roden Street, Uford, in the County of Essex, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the production of cyanine dyestuffs and particularly to the production of symmetrical dicarbo-cyanine dyestuffs containing substituents in the polymethine chain. It further relates to the sensitising of photographic emulsions.

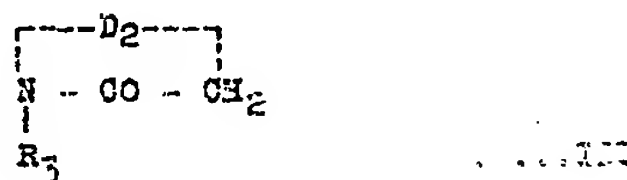
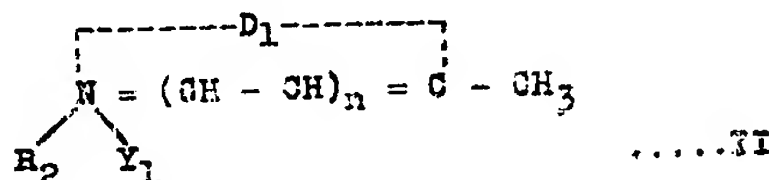
According to the present invention cyanine dyestuffs are prepared by condensing a compound of the general formula I:—



where R_1 is a nitrile (CN), a carboxylic ester (COOR) group and X is a thioether ($-\text{SR}$) or anil ($-\text{NR}$) group, R being a hydrocarbon group, e.g. an alkyl group of 1 to 4 carbon atoms or an aryl group of 6 to 10 carbon atoms with a heterocyclic

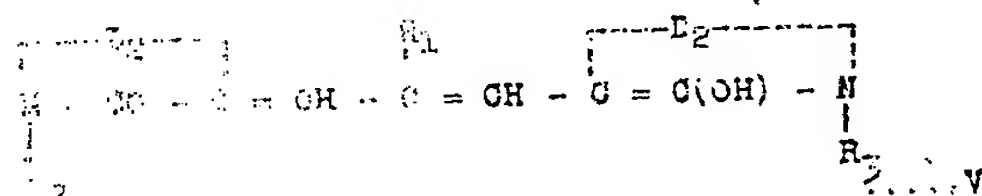
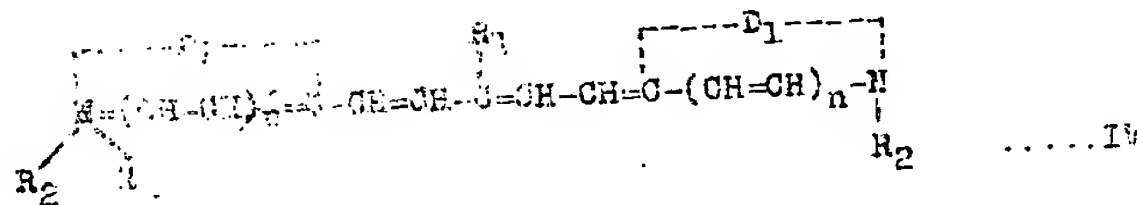
nitrogen compound containing a reactive methylene group.

More particularly, according to this invention, the said heterocyclic compound 30 conforms to one or other of the following general formulae II and III:—



where R_2 is an alkyl, hydroxyalkyl or aralkyl group, Y_1 is an acid radical, D_1 is the residue of a five-membered or six-membered heterocyclic ring, n is nought or one, R_3 is a hydrogen atom or an alkyl, aralkyl or aryl group and D_2 is the residue of a heterocyclic nitrogen-keto-methylene nucleus.

Accordingly as compounds of formulae II or III are employed, so the products conform to formulae IV or V:—



The condensation may be effected in the presence of a base or in the presence of an acid anhydride together with a base. A base such as pyridine is suitable, but it is preferred to use an organic base such as triethylamine or sodium acetate in conjunction with a carboxylic acid anhydride such as acetic anhydride.

As already indicated R_1 may be a nitrile group or a carboxylic ester group. Examples of the latter are groups of the form $-\text{COOR}$ where R is an alkyl, e.g. methyl, ethyl, propyl, butyl or higher alkyl group, or an aryl group, e.g. benzyl or naphthylmethyl, or an aryl group, e.g. phenyl or naphthyl. R_2 may be any of

the foregoing alkyl or aralkyl groups, or may be a hydroxyalkyl group such as β -hydroxy ethyl or γ -hydroxy propyl. Where R_2 is an hydroxyalkyl group this will usually be acylated by the acid condensing agent so that R_2 in the product will be an acyloxyalkyl group. R_3 , if not a hydrogen atom, may be any of the foregoing alkyl, aralkyl or aryl groups.

Y_1 may be any acid radical, for example halide (chloride, bromide, iodide), sulphate, sulphonate, perchlorate or p -toluene sulphonate.

D_1 may be the residue of any five-membered or six-membered heterocyclic ring system including thiazoles, oxazoles, selen-

azoles and their polycyclic homologues such as those of the benzene, naphthalene, acenaphthene and anthracene series; pyridine and its polycyclic homologues, such as quinoline and α - and β -naphthoquinolines, lepidines; indolenines; diazines such as pyrimidines and quinazolines; diazoles (e.g. thio- $\beta\beta'$ -diazole); oxazolines, thiazolines and selenazolines. The polycyclic compounds of these series may be substituted in the carbocyclic rings with one or more groups such as alkyl, aryl, amino, hydroxy, alkoxy and methylene dioxy groups, or by halogen atoms.

It may be the residue of rhodanic acid (2-thio-4-keto-tetrahydrothiazole), oxarhodanic acid (2-thio-4-keto-tetrahydro-oxazole) and the N-hydrocarbon substituted derivatives of such compounds, oxindoles, pyrazole- β -ones, hydantoin, thio-hydantoin, pseudohydantoin and pseudothiohydantoin.

The initial starting compounds of general formula I may be prepared by reacting a compound of the formula CH_3R , i.e. acetonitrile or an acetic ester, with a formic ester (preferably ethyl formate) in the presence of powdered sodium. This yields the compound $\text{R}-\text{CH}_2-\text{COO}$ as its sodium salt. This product is then reacted with a mercaptan RSH in the presence of dry hydrochloric acid and is reacted with aniline to produce the thioether or anil of the formula $\text{R}-\text{CH}_2-\text{S}-\text{NH}_2$. This latter compound is reacted further with a formic ester (preferably ethyl formate) and powdered sodium to yield a product of the formula II as required for use in the present invention.

The reaction is preferably effected using one molecular equivalent of the compound of formula I with substantially two molecular equivalents of the compound of formula II or III, by heating the reagents together concurrently at the boiling point of the ester or acid anhydride employed, e.g. 100 to 150° C.

Many of the dyestuffs formed according to this invention are sensitising dyes for silver and photographic emulsions.

The following illustrate the preparation of compounds of general formula I:—

55 A. PREPARATION OF α -CARBETHOXY MALON- ALDEHYDE MONO ANIL.

10 parts of sodio formyl ethyl acetate were dissolved in 100 parts of water and added with stirring to a solution of 7 parts of aniline in a mixture of 40 parts of acetic acid and 100 parts of water. The ethyl-anilinomethylene acetate was precipitated as a flocculent yellow solid. M.p. 100°.

This preparation is analogous to that of v. Pechmann, Berichte der Deutschen Chemischen Gesellschaft, 25, 1047.

A suspension of 30 parts of the above ethyl-anilinomethylene acetate in 100 parts of dry ether and 11.7 parts of ethyl formate was added in portions to 3.62 parts of sodium powder under 200 parts of dry ether. A slight reaction ensued and afterwards the solution was refluxed for 8 hours and then poured into water under an atmosphere of CO_2 . The water was ether extracted, the extracts dried over sodium sulphate and the ether removed by distillation. The product was distilled under reduced pressure, b.pt. 197° at 8 mm. pressure to give an oil which solidified on cooling to a yellow crystalline mass.

B. PREPARATION OF ETHYL- α -FORMYL- β - ETHYLTHIO ACRYLATE. 85

14 parts of sodio formyl ethyl acetate and 25 parts of ethyl mercaptan were mixed together with 25 parts of dry ether, and dry HCl gas passed through the mixture for 2 hours with cooling. After being allowed to stand overnight, the solution was poured into dilute sodium carbonate solution, ether extracted, dried over sodium sulphate anhydrous, and the ether evaporated. Distillation under reduced pressure yielded β -ethylthio ethyl acrylate. B.pt. 160—165° at 30 mm. pressure.

11 parts of the above β -ethylthioethyl acrylate and 6 parts of ethyl formate were mixed with a little dry ether and reacted with 1.5 parts of sodium powder also under dry ether. After addition the mixture was heated for 24 hours and poured into water under an atmosphere of carbon dioxide. The aqueous liquors were acidified with acetic acid, ether extracted, the extracts being washed with water, dried and the ether removed by distillation. Distillation under reduced pressure yielded crude ethyl- α -formyl- β -ethylthio acrylate. B.pt. 110—135° C. at 7 mm. pressure.

C. PREPARATION OF α -(*n*-PROPYL CARB- OXY) MALONALDEHYDE MONO ANIL. 115

13 parts of sodio formyl-*n*-propyl acetate were dissolved in 66 parts of water and added with stirring to a solution of 8 parts of aniline in a mixture of 43 parts of acetic acid and 186 parts of water. The *n*-propyl-anilinomethylene acetate was precipitated as a slightly sticky yellow solid.

A suspension of 51 parts of the above *n*-propyl-anilinomethylene acetate in 100 parts of dry ether and 20 parts of ethyl formate was added in portions to 5 parts

of sodium powder under 200 parts of dry ether. The mixture was stirred for 8 hours and then poured into water under an atmosphere of CO₂. The ether was then evaporated and the product filtered from the aqueous solution. It was a yellow solid, m.pt. 132°.

D. PREPARATION OF α-CARBOXY-MALEON-DIALDEHYDE MONO ANIL.

- 10 30 parts of sodio formyl acetone nitrile were dissolved in 200 parts of water and added with stirring to a solution of 30 parts of aniline in a mixture of 100 parts of acetic acid and 700 parts of water.
- 15 The anilinomethylene acetone nitrile was precipitated slowly as a yellow solid. M.pt. 119°.

A suspension of 7 parts of the above anilinomethylene acetone nitrile, 50 parts of dry ether and 4 parts of ethyl formate was added in portions to 1.1 parts of sodium powder under 100 parts of dry ether. After complete addition the mixture was refluxed for 4 days and then poured into water under an atmosphere of CO₂. The ether was evaporated and the product filtered as a yellow solid. After crystallisation from ethyl alcohol it melted at 183°.

- 30 The following Examples serve to illustrate the invention:—

EXAMPLE 1

BIS-2(3-ETHYL BENZTHIAZOLE)-γ-CARBETHOXY PENTAMETHINE CYANINE IODIDE.

- 35 Method (i). 10 parts of α-carbethoxy malondialdehyde mono anil, 50 parts of 2-methyl benzthiazole β-hydroxy ethiodide and 100 parts of pyridine were heated together for 3 minutes when the solution turned dark red. 6 parts of triethylamine were added with shaking and the solution allowed to cool before pouring into water. The dyestuff crystallised, was filtered and recrystallised from methyl alcohol to give dark green crystals. M.pt. 230° with decomposition.

Method (ii). 2 parts of ethyl-α-formyl-β-ethylthio acetone, 1 part of 2-methyl benzthiazole and 10 parts of pyridine were heated together for 15 minutes, during which time a deep blue colour was formed. This solution was poured into water when the dyestuff crystallised as blue-green crystals. These were well washed, dried and recrystallised from methyl alcohol. M.pt. 230° with decomposition.

This dyestuff, when incorporated in a gelatino silver bromide emulsion, imparts a band of sensitivity extending to 6800 Å with a maximum at 6400 Å.

EXAMPLE 2

BIS-2-(1-ETHYL QUINOLINE)-γ-CARBETHOXY PENTAMETHINE CYANINE IODIDE.

10 parts of α-carbethoxy malondialdehyde mono anil, 30 parts of quinaldine ethiodide and 200 parts of pyridine were heated together for 3 minutes when the solution turned red-green. 6 parts of triethylamine were added and the solution refluxed for 30 minutes, during which time a green colour slowly appeared. The pyridine solution was poured into water when the dyestuff crystallised. Recrystallisation from methyl alcohol gave blue-green crystals. M.pt. 253° (decomposition).

This dyestuff, when incorporated in a gelatino silver bromide emulsion, imparts a band of sensitivity extending to 807200 Å with a maximum at 6990 Å.

EXAMPLE 3

BIS-2-(1,3,3-TRIMETHYL-INDOLENINE)-γ-CARBETHOXY PENTAMETHINE CYANINE IODIDE.

10 parts of α-carbethoxy malondialdehyde mono anil, 30 parts of 2,3,3-trimethyl indolenine methiodide and 200 parts of pyridine were reacted as in the above Examples. The dyestuff was obtained as dark green-blue crystals upon dilution with water which, when recrystallised from methyl alcohol, melted at 207° (decomposition).

EXAMPLE 4

BIS-2(3-β-ACETOXYETHYL BENZTHIAZOLE)-γ-CARBETHOXY PENTAMETHINE CYANINE IODIDE.

10 parts of α-carbethoxy malondialdehyde mono anil, 31.6 parts of 2-methyl benzthiazole β-hydroxy ethiodide and 100 parts of acetic anhydride were heated together for 2 minutes when the colour of the solution attained a deep red. The solution was then cooled to 100°. 2 parts of triethylamine added with shaking, and the blue solution allowed to cool slowly. The dyestuff was obtained by precipitation with ether, washing with water and subsequent treatment with acetone. The dark blue solid obtained melted at 110°.

EXAMPLE 5

BIS-2(3-β-ACETOXYETHYL-5-CHLORO-BENZTHIAZOLE)-γ-CARBETHOXY PENTAMETHINE CYANINE IODIDE.

10 parts of α-carbethoxy malondialdehyde mono anil, 34 parts of 2-methyl-5-chloro benzthiazole β-hydroxy ethiodide and 100 parts of acetic anhydride were heated together and treated as in the above example. The dyestuff isolated as previously was obtained as dark green powdery crystals. M.pt. 154°.

EXAMPLE 6

BIS-2-(3-β-ACETOXYETHYL BENZTHIAZOLE)-γ-
(n-PROPYL-CARBOXY) PENTAMETHINE
CYANINE IODIDE.

- 5 2.00 parts of α-n-propyl carboxy malon-
dialdehyde mono anil, 3.1 parts of 2-
methyl benzthiazole-β-hydroxy ethiodide
and 20 parts of acetic anhydride were
heated together for 3 minutes. The solu-
10 tion was then cooled to 100°, 1.5 parts
of triethylamine added with shaking, and
the blue solution then cooled rapidly to
room temperature. Excess ether was
added to precipitate the dyestuff as a tar
15 which was washed with water and then
treated with acetone to give the crystal-
line dyestuff. This was recrystallised
from methyl alcohol to give dark blue-
green crystals. M.pt. 150° (decomposi-
20 tion).

The dyestuff, when incorporated in a
gelatine silver bromide emulsion, imparts
a weak band of sensitivity extending to
6500 Å with a maximum at 6500 Å.

EXAMPLE 7

BIS-2-(3-β-ACETOXYETHYL QUINOLINE)-γ-(n-
PROPYL-CARBOXY) PENTAMETHINE CYANINE
IODIDE.

- 25 2.50 parts of α-n-propyl carboxy
malondialdehyde mono anil, 3.1 parts of
quinoline-β-hydroxy ethiodide and 20
parts of acetic anhydride were heated
together and 1.5 parts of triethylamine
added. The procedure was similar to that
35 of the previous example. The dyestuff
was obtained after crystallisation from
methyl alcohol, as dark blue-green
crystals. M.pt. 124° (decomposition).

EXAMPLE 8

BIS-2-(3-ETHYL BENZTHIAZOLE) - γ - CYANO
PENTAMETHINE CYANINE IODIDE.

- 40 1.1 parts of α-cyano-malondialdehyde
mono anil, 3 parts of 2-methyl benz-
thiazole ethiodide and 40 parts of acetic
anhydride were heated together for 5
minutes during which time the colour
of the solution deepened to dark red. 1.6
parts of triethylamine were then added,
and after another 3 minutes' refluxing,
50 during which time a blue colour appeared,
the solution was cooled and the dyestuff
obtained. When recrystallised from methyl
alcohol it was obtained as dark brown
crystals with a green reflex. M.pt. 268°
55 (decomposition).

The dyestuff when incorporated in a
gelatine silver bromide emulsion, imparts
a weak band of sensitivity extending to
6500 Å with a maximum at 6350 Å.

EXAMPLE 9

α,γ-BIS-3-ETHYL-2-CYANO-4-KETO - TETRA-
METHYLENE-β-CYANO PROPENE.

- 60 1.1 parts of α-cyano-malondialdehyde
mono anil, 2.1 parts of N-ethyl rhodanic
acid and 20 parts of acetic anhydride were

heated together for 5 minutes. 1.4 parts
of triethylamine were then added and
heating continued for 15 minutes, during
which time the dye colour (dark green-
blue) gradually appeared. The solution 70
was cooled and the dyestuff filtered. Re-
crystallisation from methyl alcohol gave
blue crystals with a bright reflex. M.pt.
220° (decomposition).

EXAMPLE 10.

BIS-2-(3-β-ACETOXYETHYL BENZTHIAZOLE)-
γ-CYANO PENTAMETHINE CYANINE IODIDE.

- 1.7 parts of α-cyano malondialdehyde
mono anil, 6.12 parts of 2-methyl benz-
thiazole-β-hydroxy ethiodide and 30 parts 80
of acetic anhydride were heated together
for 5 minutes. 1 part of triethylamine
added, and the solution refluxed for a
further 3 minutes. The dyestuff was
filtered, after cooling the solution, and 85
recrystallised from methyl alcohol when
it was obtained as dark blue crystals.
M.pt. 243° (decomposition).

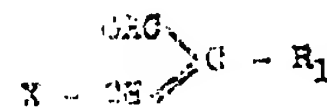
EXAMPLE 11

BIS-2-(3-ETHYL BENZSELENIAZOLE) - γ - CARB- 90
ETHOXY PENTAMETHINE CYANINE IODIDE.

- 19.6 parts of 2-methyl benzselenazole
and 18.6 parts of methyl-p-toluene sul-
phonate were fused at 100° C. for 3 hours,
10 parts of α-carboxy malondialdehyde 95
mono anil and 200 parts of acetic anhy-
dride were added, and the mixture boiled
for 30 minutes. Excess triethylamine was
then added with cooling, whereupon the
dyestuff was formed and precipitated from 100
the blue solution as a tar. This on treat-
ment with acetone gave green crystals of
the dyestuff, m.pt. 150° C. (with decom-
position).

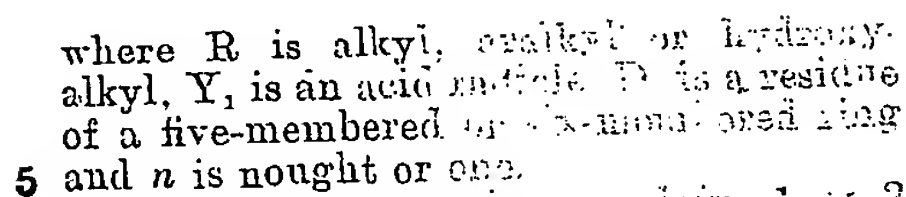
Having now particularly described and 105
ascertained the nature of our said inven-
tion and in what manner the same is to
be performed, we declare that what we
claim is:—

1. Process for the preparation of 110
cyanine dyestuffs which comprises con-
densing a compound of the general
formula:—



where R₁ is a nitrile (CN) or carboxylic 115
ester (COOR) group and X is a thioether
(SR) or aryl (C₆H₅) group, R being a
hydrocarbon group, with a heterocyclic
nitrogen compound containing a reactive
methylene group.

2. Process according to claim 1 where- 120
in the heterocyclic compound containing
a reactive methylene group is a compound
of the general formula:—



where R is alkyl, aralkyl or hydroxyalkyl, Y₁ is an acid anhydride, P is a residue of a five-membered or six-membered ring and n is nought or one.

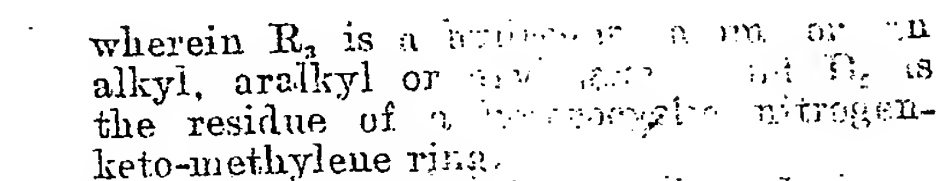
3. Process according to claim 1 or 2 wherein the reaction is effected by heating the reagents in the presence of a base.

4. Process according to any of the preceding claims wherein the reaction is effected by heating the reagents in the presence of a carbonyl acid anhydride and a strong base.

5. Process according to claim 4 where-
15 in the anhydride employed is acetic anhy-
dride and the base is triethylamine.

6. Process according to any of claims 2 to 5 wherein the residue R₁ is the residue of a benzthiazole, quinoline or indole nucleus.

7. Process according to claim 3 wherein the heterocyclic compound containing a reactive methylene group is a compound of the general formula —

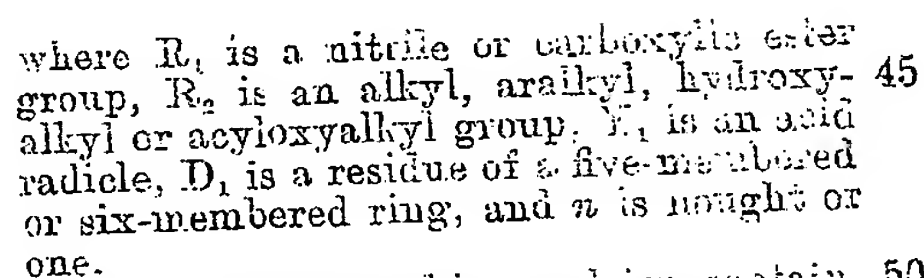


30 S. Process according to Example 1 where-
in the residue R is the residue of a
rhodanic acid anion.

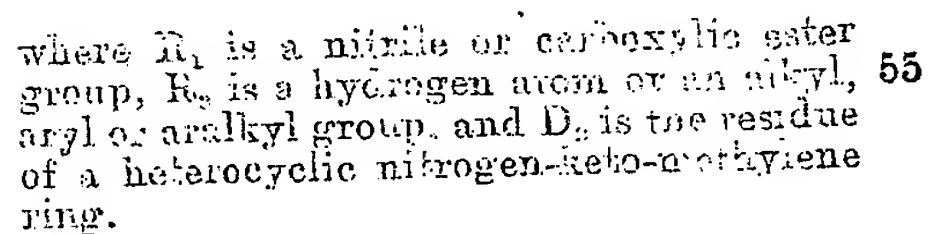
9. Process for the production of a
cyanine dyestuff substantially as set forth
in any one of the foregoing specific 25
Examples 1 to 11.

10. Cyanine dyestuffs wherever prepared or produced by any of the processes hereinbefore described and claimed.

11. A photographic emulsion contain- 40
ing in sensitising amount a dyestuff of
the general formula:—



12. A photographic emulsion contain- 50
ing in sensitising amount a dyestuff of
the general formula:—



where R_1 is a nitrile or carboxylic ester group, R_2 is a hydrogen atom or an alkyl, aryl or aralkyl group, and D_2 is the residue of a heterocyclic nitrogen-keto-methylene ring. 55

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